SYNTHESIS AND REACTIVITY OF NEW BIMETALLIC OXYNITRIDES

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ABSTRACT

A new series of catalysts, transition metal bimetallic oxynitrides of the form $M_1M_2O_xN_y$ (M_1 = V, Nb and Cr, M_2 = Mo), was prepared. The catalysts were synthesized by nitriding the bimetallic oxide precursors in an ammonia gas stream at 1000 cm^3/min (6.8×10^2 $\mu mols^{-1}$) using a heating rate of 5 K/min (8.3×10^{-2} Ks^{-1}). The catalysts were characterized by x-ray diffraction, CO chemisorption and surface area measurements. The activity of these catalysts for hydroprocessing was studied in a three-phase trickle bed reactor operated at 3.1 MPa and 643 K. The liquid feed consisted of 3000 ppm sulfur (dibenzothiophene), 2000 ppm nitrogen (quinoline), 500 ppm oxygen (benzofuran), 20 wt% aromatics (15 wt% tetralin and 5 wt% amylbenzene) and balance aliphatics (tetradecane). The activities of the bimetallic oxynitrides were compared to a commercial Ni-Mo/Al_2O_3 (Shell 324) catalyst tested at the same conditions. The bimetallic oxynitrides were found to be active for the hydrodenitrogenation (HDN) of quinoline. In particular, V-Mo-O-N exhibited higher HDN activity than the commercial Ni-Mo/Al_2O_3 catalyst. The hydrodesulfurization (HDS) activity of the bimetallic oxynitrides ranged from 9-25% with V-Mo-O-N showing the highest HDS activity among the oxynitrides tested.

INTRODUCTION

Monometallic nitrides have been investigated extensively since the 50's and 60's [1,2]. However, in order to take advantage of the catalytic properties of the carbides and nitrides, it is important to prepare these materials in high surface area form. Conventional powder metallurgy methods such as direct nitridation or carburization of metal or metal oxide powders resulted in compounds of typically low surface area (< 10 m^2g^{-1}). Significant progress has been made in the preparation of these materials in high surface area form in the last decade and a half [3-6]. One of the techniques developed during this period was the temperature programmed reaction [7] method of preparing high surface area compounds from oxide precursors. The technique offers the advantage of lower synthesis temperatures than the conventional methods. In addition, the transformation of the oxide to the carbide/nitride phase is direct, bypassing the metal phase, which is the most prone to sintering. However, most of the work on the temperature programmed reaction is focused on the synthesis of monometallic carbides and nitrides. There is little work reported on the preparation of high surface area mixed transition metal nitrides/oxynitrides in the literature.

Transition metal carbides and nitrides were found to be active for a number of hydrocarbon reactions [8]. One of the major applications of transition metal carbides and nitrides has been in hydroprocessing. Removal of nitrogen and sulfur from petroleum feedstocks is gaining importance with the need to process heavier resources. Nitrogen removal is always accompanied by the consumption of excess hydrogen due to the difficulty involved in the C-N bond scission. The development of catalysts that are selective to C-N cleavage is an important goal, and this paper reports an investigation on a new class of catalysts which is different in structure and properties from the conventional Ni-Mo/Al_2O_3 and Co-Mo/Al_2O_3 hydrotreating catalysts.

After the initial results by Schlatter, et al., [9] on quinoline HDN, most of the hydroprocessing work has been concentrated on molybdenum nitride catalysts, both supported and unsupported [10-14]. This paper reports a new family of nitrides, where the nitrogen is partially exchanged by oxygen and a second transition metal is also introduced in the interstitial compound.

SYNTHESIS AND CHARACTERIZATION

The bimetallic oxynitrides were prepared by nitriding the bimetallic oxide precursors using the temperature programmed reaction technique [15]. The oxide precursor was loaded in a quartz reactor placed in a furnace (Hoskins 500W). Ammonia reactant gas was passed over the oxide bed at a flow rate of 1000 cm^3/min (680×10^2 $\mu mols^{-1}$). The temperature of the reactor bed was ramped linearly at 5 K/min (8.3×10^{-2} Ks^{-1}) to the final synthesis temperature (T_{max}) and held at that temperature for a period of time (t_{hold}). The effluent gases from the reactor were analyzed by an on-line mass spectrometer (Ametek/Dycor, MA100). Once the reaction was completed, the gas flow was switched to helium and the reactor was quickly cooled down to room temperature by removing the furnace. The catalysts were passivated at room temperature in a 0.5% O_2/He gas mixture before exposure to the atmosphere. A summary of the synthesis conditions used in the preparation of these materials is presented in Table 1.

The bulk phase purity of the samples was identified by x-ray diffraction (XRD) (Siemens Model D500 with a CuKα monochromatized radiation source). Figure 1 presents the XRD patterns of the passivated bimetallic oxynitrides. The patterns did not show any features of the starting oxide material and moreover, all the patterns indicate that the oxynitrides have a face centered cubic arrangement. In addition, the line-broadening of the peaks indicates the presence of small crystallites. Elemental analysis indicated that the actual composition of the catalysts was $V_{2.0}Mo_{1.0}O_{1.7}N_{2.4}$, $Nb_{2.0}Mo_{2.6}O_{3.0}N_{4.2}$ and $Cr_{1.0}Mo_{1.3}O_{2.3}N_{1.4}$. N_2 physisorption and CO chemisorption measurements were carried out to obtain the specific surface area and the number of exposed surface metal atoms. Prior to surface adsorption measurements, the catalysts were activated in a flow of 10% H_2/He gas mixture at 738 K for 2 h. The surface areas, CO uptakes and the number densities are summarized in Table 2. The number densities indicated in Table 2 reveal that only a maximum of 14% of the total metal atoms are available for the chemisorbing molecule. These values are typical of the interstitial compounds due to the prior occupation of the sites by N and O, which were not removed during the activation process.

REACTIVITY

Experimental runs consisted of testing a series of oxynitride catalysts for their activity in hydrodenitrogenation (HDN), hydrodesulfurization (HDS) and hydrodeoxygenation (HDO). The reactions were carried out in a three-phase trickle-bed reactor at 3.1 MPa and 643 K. Typically about 0.2-1 g of the catalyst was loaded, corresponding to a total surface area of 30 m^2. Prior to catalytic testing, the oxynitrides were activated in flowing hydrogen at 723 K for 3 hours. The commercial Ni-Mo/Al_2O_3 catalyst was sulfided in a flow of 10% H_2S/H_2 gas mixture. After the activation process, the reactors were cooled down to 643 K and hydrogen was pressurized to 3.1 MPa. Hydrogen flow to the reactor was maintained at 150 cm^3(NTP)/min (100 $\mu mols^{-1}$) using mass flow controllers. Liquid feed rate was set at 5 cm^3h^{-1} using high-pressure liquid pumps. The gas and liquid passed over the catalyst bed in a cocurrent upflow mode and out

to the liquid sampling valve. The liquid feed composition used in all the experiments was 3000 ppm S (dibenzothiophene), 2000 ppm N (quinoline), 500 ppm O (benzofuran), 20 wt% aromatics (15 wt% tetralin and 5 wt% amylbenzene) and balance aliphatics (tetradecane). The reactions were carried out for a period of 60 hours. The liquid samples were analyzed off-line by gas chromatography.

The activity of the catalysts was compared on the basis of equal surface areas of 30 m^2 loaded in the reactor. Figure 2 shows a comparison of the activities of the catalysts for HDN, HDS and HDO at 3.1 MPa and 643 K. Clearly, the oxynitrides show considerable activity for the HDN of quinoline. In fact, V-Mo-O-N exhibited higher activity than the commercial sulfided Ni-Mo/Al_2O_3 catalyst. All the catalysts showed similar product distribution and the major hydrodenitrogenated product was propylcyclohexane. The HDN activity of the catalysts was stable even after 60 hours on-stream. The HDS activity of the oxynitrides ranged from 9-25%, with V-Mo-O-N displaying the highest HDS activity among the oxynitrides tested. The oxynitrides showed high initial HDS activities, but they deactivated after about 25 h on-stream. The major product from the HDS of dibenzothiophene was biphenyl. The oxynitrides were also active for the removal of oxygen from benzofuran. The HDO activity ranged from 12-32% and the major deoxygenated product was ethylcyclohexane. In fact, the V-Mo-O-N showed higher overall activity than the corresponding monometallic nitrides [16]. The commercial Ni-Mo/Al_2O_3 catalyst showed high activities for the removal of sulfur and oxygen from the liquid feed.

X-ray diffraction patterns of the spent catalysts indicated that the bulk phase purity of the samples was preserved. The patterns did not show extraneous oxide or sulfide peaks indicating that the oxynitrides were stable towards heteroatoms even after prolonged exposure at elevated temperatures.

CONCLUSIONS

A new series of catalysts, bimetallic oxynitrides of transition metals, was prepared in high surface area form. They were found to be active for the hydrodenitrogenation of quinoline. Interestingly, V-Mo-O-N displayed higher HDN activity than the commercial Ni-Mo/Al_2O_3 catalyst. The new catalysts were found to be sulfur resistant under the reaction conditions. The bimetallic oxynitrides displayed better activity and stability than the monometallic nitrides.

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Table 1. Summary of the Synthesis Conditions

Catalyst	Final Temperature T_{max} / K	Soak Period t_{hold} / h
V-Mo-O-N	1037	0.5
Nb-Mo-O-N	1063	0.3
Cr-Mo-O-N	1013	0.3

Table 2. Results of Surface Adsorption Measurements

Catalyst	CO Uptake $\mu molg^{-1}$	Surface Area m^2g^{-1}	Number Density $\times 10^{15}$ cm^{-2}
V-Mo-O-N	167	74	0.14
Nb-Mo-O-N	11.2	121	0.0056
Cr-Mo-O-N	163	90	0.11

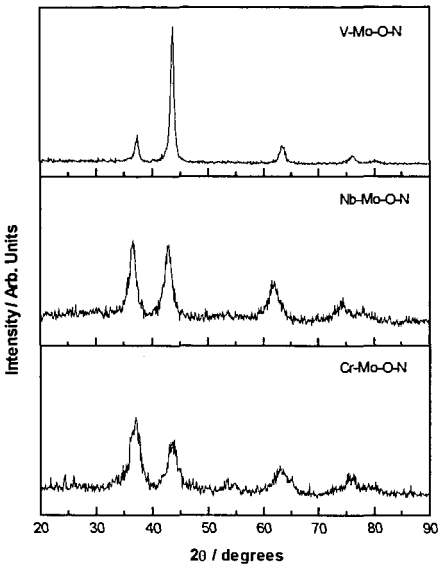

Figure 1. X-ray diffraction patterns of the fresh catalysts.

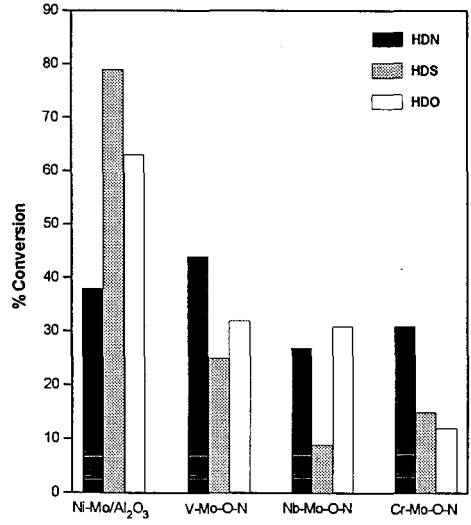

Figure 2. Comparison of the HDN, HDS and HDO activities of the catalysts at 3.1 MPa and 643 K.